

JC17 Rec'd PCT/PTO 13 JUN 2005

ENGLISH TRANSLATION OF PCT/FR03/0036695 GRADIENT COPOLYMERS SOLUBLE OR AT LEAST DISPERSIBLE
IN WATER AS WELL AS IN ORGANIC SOLVENTS

The invention relates to the field of amphiphilic copolymers, particularly to the field of amphiphilic gradient copolymers and more particularly to the field 10 of gradient copolymers which are soluble or dispersible in water as well as in organic solvents.

It also relates to a process for the synthesis of these 15 gradient copolymers and to a process for employing such polymers in solution in water or in a water/alcohol mixture at concentrations of greater than or equal to 5%.

The invention also relates to the use of such solutions 20 in formulations which can be used in different sectors of application, such as cosmetics, aqueous paints, adhesion to surfaces having little natural affinity for water, or the dispersion of inorganic fillers.

25 Generally, a polymer material may be described by the following three quantities: number-average mass, denoted below by M_n ; weight-average mass, denoted below by M_w ; and the polydispersity index PI .

30 These three quantities are sufficient to describe a homopolymer or a copolymer, provided that its chemical composition is well known. In fact, the following definitions will demonstrate that a gradient copolymer has to be described much more specifically and that the 35 parameters of its synthesis will be determining in order to describe it correctly.

In what follows, the abbreviation T_g denotes the glass

transition temperature of a polymer.

In the present invention, the term "hydrophilic monomer" will denote, without distinction, monomers 5 having corresponding homopolymers which are soluble in water or dispersible in water or having an ionic form which is soluble in water or dispersible in water.

A homopolymer is said to be soluble in water if it 10 forms a clear solution when it is in solution at 5% by weight in water at 25°C.

A homopolymer is said to be dispersible in water if, at 15 5% by weight in water at 25°C, it forms a stable suspension of fine, generally spherical, particles. The mean size of the particles constituting said dispersion is less than 1 μm and more generally varies between 5 and 400 nm, preferably from 10 to 250 nm. These particle sizes are measured by light scattering.

20 The following definitions are of use in making it possible to distinguish gradient copolymers from other copolymers and polymers:

25 Controlled radical polymerization:

- Radical polymerization controlled by nitroxides. WO 96/24620 or WO 00/71501 discloses the devices of this polymerization and their use. The scientific 30 understanding of such a control technique is described by Fischer in Chemical Reviews, 2001, 101, 3581, by Tordo and Gnanou in J. Am. Chem. Soc., 2000, 122, 5929, and Hawker in J. Am. Chem. Soc., 1999, 121, 3904, for example.

35 - Atom transfer radical polymerization. Disclosed in WO 96/30421, it proceeds by reversible insertion with regard to an organometallic complex in a bond of carbon-halogen type.

- Radical polymerization controlled by sulfur derivatives of xanthate, dithioester, trithiocarbonate or trithiocarbamate type. Reference may be made to the
5 following documents: FR 01/02848, WO 02/068550, WO 98/01478, WO 99/35177, WO 98/58974, WO 99/31144 or WO 97/01478, a reference publication in the field being: Rizzardo et al., *Macromolecules*, 1998, 31, 5559.

10

Controlled radical polymerization denotes polymerizations for which the side reactions which usually result in the disappearance of the propagating entities (termination or transfer reaction) are rendered highly
15 improbable with respect to the propagation reaction by virtue of an agent for controlling the free radicals. The shortcoming of this method of polymerization lies in the fact that, when the concentrations of free radicals become high with respect to the concentration
20 of monomer, the side reactions again become determining and tend to broaden the distribution of the masses.

Gradient

25 Gradient copolymer: the gradient copolymer is a copolymer of at least two monomers generally obtained by living or pseudoliving polymerization. By virtue of these methods of polymerization, the polymer chains grow simultaneously and thus incorporate, at each
30 instant, the same ratios of comonomers. The distribution of the comonomers in the polymer chains thus depends on the change, during the synthesis, in the relative concentrations of the comonomers. Reference will be made to the following publications for a
35 theoretical description of gradient copolymers: T. Pakula et al., *Macromol. Theory Simul.*, 5, 987-1006 (1996); A. Aksimetiev et al., *J. of Chem. Physics*, 111, No. 5; M. Janco, *J. Polym. Sci.*, Part A: *Polym. Chem.* (2000), 38(15), 2767-2778; M. Zaremski et al.,

Macromolecules (2000), 33(12), 4365-4372;
K. Matyjaszewski et al., J. Phys. Org. Chem. (2000),
13(12), 775-786; Gray Polym. Prepr. (Am. Chem. Soc.,
Div. Polym. Chem.) (2001), 42(2), 337-338;
5 K. Matyjaszewski, Chem. Rev. (Washington, D.C.) (2001),
101(9), 2921-2990.

Natural gradient: will be used for a gradient copolymer synthesized under batchwise conditions from a starting mixture of comonomers. The distribution of the various monomers in the chain thus follows a law deduced from the relative reactivity and from the starting concentrations of monomers. These polymers constitute the simplest class of gradient copolymers as it is the starting mixture which defines the final product property.

Artificial gradient: will be used for a copolymer, the concentration of monomers of which will be varied 20 during the synthesis by a processing stratagem.

Composition gradient: this is the G function defined by

$$\vec{G}(\vec{x}) = \sum \overrightarrow{[M_i](\vec{x})}$$

25 where x denotes the standardized position on the polymer chain and $[M_i](x)$ denotes the relative concentration in this position of the monomer M_i (expressed in moles). In the case of isoreactive 30 monomers, $[M_i](x) = 1/2$.

The $G(x)$ function thus describes the composition of the gradient polymer locally. Two copolymers can have an equivalent overall composition but very different $G(x)$ 35 functions. The factors determining the $G(x)$ functions are the relative reactivity coefficients of the monomers (r_i for the monomer M_i) (which depend mainly on the type of process of synthesis (homogeneous,

disperse) and on the solvents, and the like), the starting concentrations of the monomers and the additions of monomers during the polymerization. Mention may be made, by way of example, of the textbook 5 case of a gradient copolymer of styrene (M_1) and of methacrylic acid (M_2) in a homogeneous polymerization system. The literature gives us $r_1 = 0.418$ and $r_2 = 0.6$.

10 The variation in the starting concentrations of styrene and of methacrylic acid makes it possible to obtain different gradient copolymers thus having chains with completely different structures. Thus, at 10% of methacrylic acid, a very low gradient copolymer is obtained 15 for which nanostructuring cannot be expected, at 20% a copolymer with a hydrophilic "head" and a hydrophobic tail is obtained with a sufficiently pronounced gradient to result in nanostructuring. On the other hand, at 50%, the monomers being isoreactive under 20 these conditions, the copolymer obtained is of the alternating type.

Despite the fact that each of the polymers described is a gradient polymer of styrene and of methacrylic acid, 25 the difference in starting concentration of the monomers results in chains with completely different structures, conferring different properties on the copolymers.

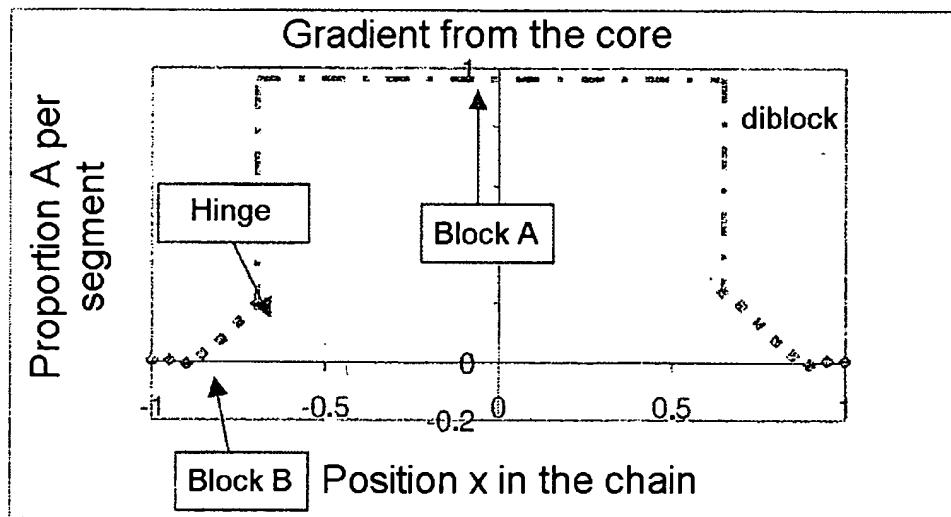
30 This example thus illustrates the importance of the starting monomer concentrations on the arrangement of the different monomers along the chain.

Block copolymer:

35 This is in fact a subclass of the family of the artificial gradient copolymers. $[M_i](x)$ is then the product of at least one Dirac function by a monotone function, which reflects the fact that the mixture of

monomers changes from one form to another in the chain due to a change undergone by the monomers in the reaction medium (stripping of the first mixture or addition of at least one new monomer). Some block 5 copolymers are distinguished in that they have a random hinge between the two blocks.

In WO 02/068550, the authors disclose and claim block polymers of $(AB)_n$ -core type (with n greater than or 10 equal to 2) with optionally a hinge between the A and B blocks; such structures correspond to the following $GA(x)$ curves:



15

It is therefore seen that the structure of such a chain is:

- symmetrical
- the notion of block is reflected by a zone at least 20 of the chain where the composition of A is 1 and of B is 0,
- such structures correspond to a process of synthesis based on the polymerization of a first mixture of monomers and then of a second with optionally 25 purification between the two stages of the polymer to avoid the hinge block.

Such compounds are nanostructures and therefore exhibit

physical and rheological properties in keeping with this nanostructuring: the order/disorder temperature is high. Up to this temperature, the viscosity of the polymer is very high and one of the consequences is 5 that it is difficult, indeed even impossible, to dissolve such polymers in aqueous solution or in a solvent.

It emerges from these definitions and from these 10 examples that the $G(x)$ functions, the number-average mass and the polydispersity index are three necessary and sufficient pieces of information which differentiate one gradient copolymer from another. It also emerges that the $G(x)$ function is directly 15 determined by the process of synthesis.

Surprisingly, the Applicant Company has discovered that 20 amphiphilic gradient polymers having at least one hydrophilic monomer and at least one monomer M_1 , the homopolymer of which corresponding to a Tg_1 of less than 20°C, exhibit the advantage of being easy to handle in water or in a solvent in comparison with block copolymers while retaining rheological properties which are advantageous for applications such as paint, 25 varnishes, adhesion, filler dispersion or even formulations for medical, dermatological or cosmetic use, it being possible for the monomer M_1 to be a hydrophilic monomer.

30 The first subject matter of the invention is a gradient copolymer comprising at least two monomers, the first (M_1), the homopolymer of which corresponding to a Tg_1 of less than 20°C, represents at least 50% by weight of the total weight of the copolymer, the second (M_2), the 35 homopolymer of which corresponding to a Tg_2 of greater than 20°C and preferably of greater than 50°C, represents at most 50% by weight of the total weight of the copolymer. Furthermore, at least one of the monomers must be hydrophilic and represent at least 5%

by weight of the total weight of the copolymer.

The copolymer of the invention comprises at least one monomer M_i such that the probability of encountering M_i 5 in any standardized position x situated along the polymer chain is nonzero.

Preferably, Tg_1 is between -150°C and 20°C and more preferably between -120°C and 15°C .

10

According to a preferred form of the invention, the hydrophilic monomer represents at least 10% by weight of the weight of the copolymer.

15

In addition, the gradient copolymer of the invention exhibits average masses of between 5000 g/mol and 1 000 000 g/mol and exhibits polydispersity indices of between 1.1 and 2.5, preferably between 1.1 and 2.

20

The hydrophilic monomers can be chosen from the following monomers, which are spontaneously hydrophilic or which are rendered hydrophilic by simple transformation (quaternization of an amine or neutralization of an acid) in the polymer structure:

25

- ethylenic carboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid or fumaric acid,

- acrylates and methacrylates of polyethylene glycol or of glycol which are or are not substituted on their end functional group by alkyl, phosphate, phosphonate or sulfonate groups,

30

- amides of unsaturated carboxylic acids, such as acrylamide or methacrylamide and their N-substituted derivatives,

- aminoalkyl acrylates and methacrylates, and aminoalkylmethacrylamides,

35

- carboxylic anhydrides carrying a vinyl bond, such as maleic anhydride or fumaric anhydride,

- vinylamides, such as vinylpyrrolidone or vinylacetamide,

- vinylamines, such as vinylmorpholine or vinylamine,
- vinylpyridine.

Preferably, M_1 is chosen from the following monomers:

5

- linear or branched C_1-C_{12} alkyl acrylates,
- polyethylene glycol (meth)acrylates,
- dienes, such as butadiene or isoprene.

10 The other monomers participating in the copolymer of the invention are chosen from the following monomers:

- styrene derivatives,
- (meth)acrylic derivatives resulting in polymers with high T_g values, such as norbornyl acrylate or methyl methacrylate,
- 15 - acrylonitrile and methacrylonitrile.

The gradient copolymers of the invention can be obtained by controlled radical polymerization, in particular according to the procedure described below:

20 1) The mixture of the monomers to be polymerized, a radical polymerization initiator and an agent for controlling the polymerization are introduced into a stirred reactor which may or may not contain a solvent. The mixture is placed under an atmosphere of a gas which is inert with respect to radical polymerization, such as nitrogen or argon. Alkyl acetates, such as, inter alia, butyl acetate or ethyl acetate, aromatic solvents, ketone solvents or alcoholic solvents will advantageously be chosen as optional polymerization solvent. In the case where the mixture of monomers is miscible with water, the latter can advantageously be used as solvent.

25 30 2) The mixture is brought with stirring to the desired polymerization temperature. This temperature is chosen within a range from $10^\circ C$ to $160^\circ C$, preferably from $25^\circ C$ to $130^\circ C$. The choice of the polymerization temperature should be optimized according to the chemical composition of the mixture of monomers. Specifically, certain monomers having very high

kinetic propagation constants and a lower affinity for the control agent must be polymerized at low temperature (for example, in the case of a significant proportion of methacrylic derivatives, 5 polymerization at a temperature of between 25°C and 80°C will be preferred).

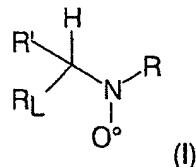
3) The polymerization medium is optionally modified during the polymerization (before achieving 90% conversion of the starting monomers) by 10 supplementary addition of one or more of the monomers of the starting mixture. This addition can be carried out in different ways, ranging from sudden addition to continuous addition over the complete duration of the polymerization.

15 4) The polymerization is halted when the desired conversion is achieved. The overall composition of the polymer and the G(x) function depend on this conversion. Preferably, more than 50% conversion will be achieved. The achievement of more than 90% 20 conversion is also preferred.

25 5) The possible residual monomers are removed, either by evaporation or by addition of an amount of conventional polymerization initiator, such as peroxide or azo derivatives.

According to the invention, the agent for controlling the polymerization is the nitroxide (I). The process according to the invention consists of the synthesis of the copolymers in the presence of nitroxides (I):

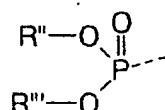
30



35 - where R' and R, which are identical or different and which are optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon

atoms which are optionally substituted by hydroxyl, alkoxy or amino groups. In particular, R and R' will be tert-butyl groups.

5 - and where R_L is a monovalent group with a molar mass of greater than 16 g/mol which can be a phosphorus or aromatic group; in particular, R_L is a phosphorus group and more particularly a phosphonate group of formula:



10

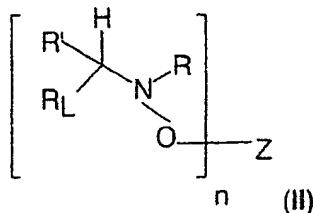
15 - where R'' and R'''', which are identical or different and which are optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms which are optionally substituted by hydroxyl, alkoxy or amino groups. In particular, R'' and R''' will be ethyl groups.

20 Conventional (azo or peroxide) polymerization initiators can be used while observing a nitroxide/initiator molar ratio of between 2 and 2.5, if it is considered that one mol of these initiators gives rise to two mol of polymer chains, or between 1 and 1.25 for monofunctional initiators.

25

Alkoxyamines of general formula (II) can advantageously be chosen to initiate the polymerization and to release, at the same time, the nitroxide which controls this polymerization,

30



where n is a integer of less than or equal to 8 and preferably of between 1 and 3 and Z is a monovalent or multivalent radical of styryl, acryloyl or methacryloyl type, the other radicals having the same meanings as above. The quality of the control of the polymerization can be improved by adding nitroxide (I) to the alkoxyamine (II) in a proportion ranging from 0 to 20 mol% with respect to the moles of alkoxyamine functional groups (one mol of polyvalent alkoxyamine contributes a number of alkoxyamine functional groups proportional to its valency).

The choice of the initiator will be dictated by the requirements of the application:

15 - a monofunctional initiator will result in asymmetric chains,
- a polyfunctional initiator will result in macromolecules having a symmetry starting from a core.

20 The choice of the hydrophilic/hydrophobic monomers will be dictated by the importance of situating the hydrophilic monomers at a precise point on the chain.

25 Thus, if it is desired for the hydrophilic units to be in the core of a polymer chain, a difunctional initiator and a mixture of monomers such that the reactivity of the hydrophilic monomers is greater than that of the hydrophobic monomers will be chosen; this is the case, for example, with methacrylic acid with 30 respect to acrylate monomers in general. In the case where the hydrophilic units are desired at the periphery, the contrary case will be chosen, such as, for example, the acrylate/vinylpyrrolidone pair.

35 The copolymers of the invention are water-soluble or water-dispersible. They are of use in formulations for paints, adhesives, glues and cosmetics. They are also of use for pigment dispersion.

One of the other subject matters of the invention is a process for the aqueous dissolution of the gradient copolymers of the invention which comprises:

- 1) Dissolving the polymer in a ketone solution at a
5 level of solid of between 20 and 90%, preferably between 20 and 50%; preferably, acetone or methyl ethyl ketone (MEK) will be chosen.
- 2) In the case of hydrophilic monomers of acid type, an at least one 1M solution of base, such as a salt of hydroxonium ion (OH^-), an amine, ammonia, a carbonate (CO_3^{2-}) salt or a hydrogencarbonate (HCO_3^-) salt, is added to the vigorously stirred solution.
10 In the case of hydrophilic monomers of amine type, an at least 1M solution of acid, such as hydrochloric acid, hydrobromic acid, hydriodic acid, acetic acid, propionic acid, sulfuric acid, phosphoric acid or hydroboric acid, is added. In the case of neutral hydrophilic monomers, such as dimethylacrylamide or vinylpyrrolidone, the solution
15 obtained in 1 is left unchanged.
- 3) Water is then added, with vigorous stirring, to the solution obtained in 1 or optionally in 2 in a proportion such that the level of solid obtained is between 1 and 80%. Optionally, the water can be
20 replaced by water/alcohol mixtures in proportions ranging from 99/1 to 50/50.
- 4) The ketone is evaporated by conventional evaporation techniques, in particular by stirring the solution at 100°C. Concentrating is continued until the
25 desired level of solid is obtained.

30 This is because the Applicant Company has noticed that, in order to succeed in the aqueous dissolution of such polymers, it was advisable for the latter to be first
35 dissolved in an organic solution.

Another subject matter of the present invention relates to the use of such polymers in solution in water or in a water/alcohol mixture at concentrations greater than

or equal to 5%. The aqueous or organic solutions of such polymers also form part of the invention.

The invention also relates to the use of such solutions
5 in formulations which can be used in various sectors, such as cosmetics, paints, adhesion to surfaces having little natural affinity for water, or the dispersion of inorganic fillers.

10 The following examples illustrate the invention without limiting the scope thereof.

Characterization of the polymers:

15 The molar masses and their distribution were determined by steric exclusion chromatography (SEC) by universal calibration using polystyrenes as standard and the Mark-Houwink coefficients of PMMA for the copolymers.

20 The chemical composition of the copolymers can be determined by proton NMR, UV spectrometry or infrared spectrometry.

25 The experimental characterization of the gradient is provided by the measurement during polymerization of the chemical composition of the polymer.

This is because, for the polymers prepared by living or pseudoliving polymerization, the length of the chains
30 is linearly related to the conversion. In other words, if it is known what proportion of a monomer M_1 is incorporated at a given moment of the polymerization, the length which the chains will have at this moment of the polymerization will be known and thus the function
35 $[M_2](x)$, where x is the position with respect to the total length of the chain, can be determined.

By withdrawing samples at different instants of the polymerization and by determining the difference in

content of each monomer, the gradient is thus established.

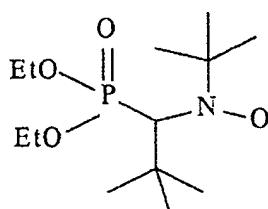
Another method for determining the gradient function is
5 the measurement, as the monomers are converted, of the Tg of the polymer. This is because, to a first approximation, the Tg can be estimated by the relationship:

10 $\frac{1}{Tg} = \sum \frac{x_i}{Tgi}$, where Tgi denotes the Tg of the homopolymer
of the monomer i and xi its mass fraction.

These methods reflect the average chemical composition
15 of the material obtained by polymerization. In addition, it is important to demonstrate that all the chains of polymers have an analogous composition. For this, use will advantageously be made of liquid absorption chromatography, which makes it possible to separate the polymer chains no longer according to
20 their molecular weight but according to their polarity. The latter reflects the chemical composition of the polymers constituting the material.

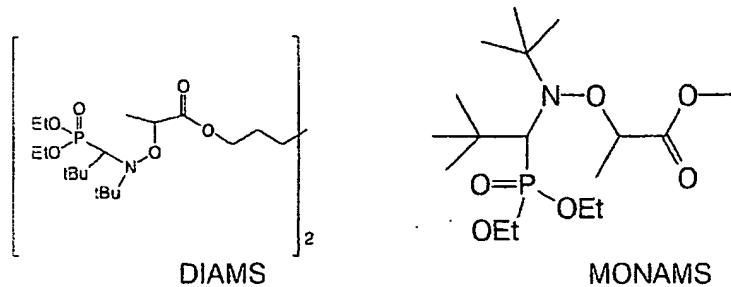
Initiators and control agent used:

25 The stable free radical used as polymerization control agent in the examples and referenced SG1 corresponds to the following formula:



30

The alkoxyamines DIAMS and MONAMS mentioned in the examples correspond to the following formulae:



Relative reactivity coefficients of some monomers used:

Some of the relative reactivity coefficients used in
5 the examples are given in table 1:

Table 1: Reactivity coefficients r_1 , r_2 of the pairs of monomers M_1/M_2

	M2								
M1	\	EA	S	MMA	MAA	AA	Maleic anhydride	NVP	
	EA	1	0.18	0.11	0.31	0.91	/		
	S	0.84	1	0.478	0.418	0.25	0.01	17	
	MMA	2.8	0.585	1	1.28	/	5.2		
	MAA	1.25	0.6	0.48	1	/	/		
	AA	1.31	0.136	/	/	1			
	Maleic anhydride			0.02	0.02	/	/	/	
	NVP		0.05						

10 NVP N-Vinylpyrrolidone
EA Ethyl acrylate
S Styrene
MMA Methyl methacrylate
AA Acrylic acid
15 MAA Methacrylic acid

Example 1: bulk synthesis of gradient copolymer

The mixture of reactants is as follows:
20 - MONAMS: 3.0 g
- SG1: 0.18 g

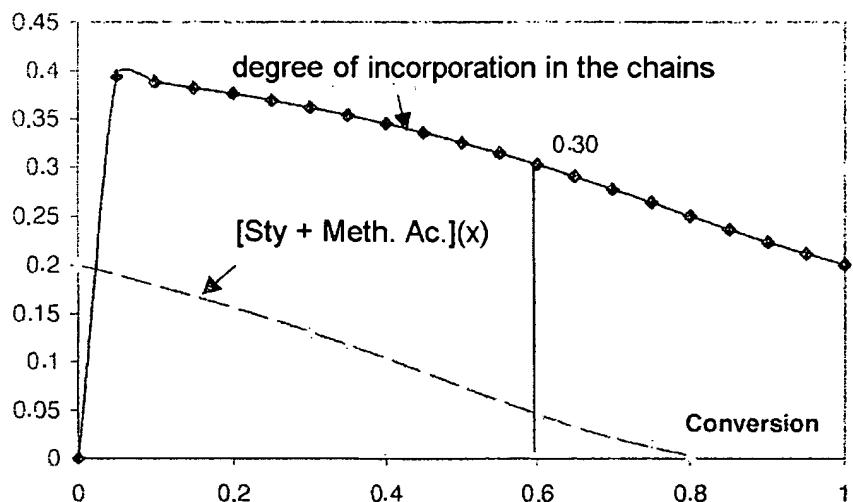
- Ethyl acrylate (EA): 480 g i.e. 80% by weight/
total weight of monomers
- Styrene (S): 60 g i.e. 10% by weight/
total weight of monomers
- 5 - Methacrylic acid (MAA): 60 g i.e. 10% by weight/
total weight of monomers

All the constituents are mixed, in the absence of solvent, under a nitrogen atmosphere, and are then heated at a temperature maintained between 110 and 115°C for 198 minutes.

The calculation of the gradient by simulation gives the curve below. The validity of this model is given by the monitoring of the relative concentrations of the three monomers by gas chromatography and NMR analysis of the polymers.

It is found that, at 60% conversion, the chemical composition of the copolymer is: 68.4% ethyl acrylate, 16.1% styrene and 15.5% methacrylic acid, according to NMR on the calculated curve (69%).

25 Incorporation of the STY,MAA mixture as a function
of the conversion (level of starting acrylate: 80%)



STY and MAA in the above figure respectively indicate Styrene and Methacrylic Acid.

The final composition of the copolymer is as follows:

- ethyl acrylate: 68.4% by weight,
- styrene: 16.1% by weight,
- 5 - methacrylic acid: 15.5% by weight.

By LAC, the plot of the polymer shows a low polydispersity of the chemical composition of the chains.

10 The measurement of the masses by steric exclusion chromatography leads to the following results:
 $M_n = 32\ 140\ g/mol$ and $M_w = 51\ 700\ g/mol$, giving a polydispersity index $PI = 1.6$.

15 A diagrammatic representation of the copolymer obtained may be as follows:



20 in which the dark spheres denote the styrene/methacrylic acid sequences and the white spheres denote the ethyl acrylate sequences.

Example 2: bulk synthesis of gradient copolymer

25 Different copolymers were prepared, according to the procedure described in example 1, from the following mixture of reactants:

- MONAMS: 3.0 g
- 30 - SG1: 0.18 g
- Styrene: 60 g
- Methacrylic acid: 60 g
- Acrylate (or mixture of acrylate): 480 g

Ex- ample	Acrylate	Characteristics of the copolymer	Final composition of the copolymer (% by weight)
2a	Butyl acrylate (BuA)	Mn = 31 100 g/mol Mw = 52 930 g/mol PI = 1.7	Styrene: 18 Methacrylic acid: 22 Butyl acrylate: 60
2b	Methyl acrylate (MeA)	Mn = 32 750 g/mol Mw = 61 470 g/mol PI = 1.88	Styrene: 20 Methacrylic acid: 21 Methyl acrylate: 59
2c	50/50 by weight butyl acrylate/ ethyl acrylate (EA) mixture	Mn = 29 690 g/mol Mw = 51 630 g/mol PI = 1.74	Styrene: 18 Methacrylic acid: 16 Acrylates: 66

Example 3: synthesis in the presence of solvent

- 5 The same synthesis is carried out as in example 1 but in the presence of solvent. The mixture of reactants is as follows:
 - MONAMS: 3.43 g
 - SG1: 0.2 g
- 10 - Ethyl acrylate: 336 g
 - Styrene: 42 g
 - Methacrylic acid: 42 g
 - Toluene: 180 g
- 15 All the constituents are mixed, in toluene as solvent, under a nitrogen atmosphere, and are then heated at a temperature maintained between 110 and 115°C for 198 minutes.
- 20 The final degree of conversion is 82% and the level of solid obtained is 57.2% by weight.

The analytical results below are determined:

Mn = 30 570 g/mol, Mw = 50 500 g/mol and PI = 1.65.

25

The final composition of the copolymer is given by

liquid absorption chromatography (LAC), which shows the similarity in composition with the copolymer prepared in example 1 and the absence of homopolymer in the materials. This is illustrated by curve 1 above given
5 in example 1.

Example 4: synthesis in the presence of solvent

10 The synthesis of a new copolymer is carried out according to the process of example 3 but in a different solvent: methyl ethyl ketone.

The starting composition of the mixture is:

- MONAMS: 4.893 g
- 15 - SG1: 0.2881 g
- Ethyl acrylate: 293.8 g
- Methyl acrylate: 32.66 g
- Styrene: 76.8 g
- Methacrylic acid: 76.8 g
- 20 - Methyl ethyl ketone: 120 g

The final degree of conversion is 99% and the level of solid obtained is 79.9%.

25 The analytical results below are determined:

$M_n = 30\ 500\ g/mol$

$M_w = 58\ 000\ g/mol$

$P_I = 1.9$

30 The incorporation of the monomers over time is measured by monitoring, by gas chromatography, the levels of residual monomers over time:

Time	0	75	130	190	290	400
Overall conversion	0	16	30.5	49.5	85.4	99
Residual monomers (%)	MeA	5.45	5.1	3.75	3.75	1.6
	EA	48.95			17.95	1.2
	MAA	12.8	12.15	4.6	2	0.35
	S	12.8	12.46	6.7	3.92	0.15
						0.007

*The total level of residual monomers is calculated taking into account the solvent quantified by the level of solid.

5

It is noted that each monomer is present throughout the reaction.

The final composition of the copolymer is as follows:

10 - ethyl acrylate: 34% by weight
- methyl acrylate: 34% by weight
- styrene: 16% by weight
- methacrylic acid: 16% by weight

15 **Example 5**

An aqueous solution, with a level of solid of 10%, of the copolymer prepared in example 2a is prepared.

20 To do this, the polymer is dried beforehand in an oven. 10 g of polymer are then dissolved in 90 ml of water comprising 1.6 g of AMP (2-amino-2-methylpropanol). A clear and very fluid aqueous dispersion is obtained. The size of the particles, measured by scattering
25 (Coulter 4NW device), is 33 nm.

Example 6

An aqueous solution of the copolymer prepared in
30 example 1 is prepared.

10 g of polymer are dissolved in 40 g of tetrahydrofuran; 1.41 g of AMP (2-amino-2-methylpropanol),

dissolved in 10 ml of water, are added. The solution thickens. 90 ml of demineralized water are then added slowly and with vigorous stirring. The solution remains clear and becomes fluid again.

5

The solvent is evaporated and a clear and fluid aqueous dispersion is obtained. The size of the particles, measured by scattering (Coulter 4NW device), is 199 nm.

10 **Example 7:** example of the use of a gradient copolymer solution in the manufacture of solvent or aqueous gels.

10 g of the copolymer of example 2b are diluted in 90 g of methyl ethyl ketone. 0.8 g of propyldiamine is added
15 to the medium with stirring and a gel is instantaneously obtained.

10 g of the copolymer of example 7 are diluted in 90 ml of methyl ethyl ketone. 2 g of ethanol diisopropylamine
20 are added to the medium. The medium remains fluid. 180 g of water are added to this solution. An aqueous gel is obtained.